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Bottom ash characterization and its catalytic potential in biomass gasification

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Abstract

Biomass gasification has received much attention in recent years due to efforts in finding alternatives to fossil fuels. However the inefficiencies of the process and also the by-product produced during the gasification makes this process unsuitable for commercial applications. Thus, catalyst is used to improve the product gas quality and to reduce the tar formation. Commercial catalyst such as dolomite, nickel and olivine are widely used in biomass steam gasification, but it has limitation such as short active lifetime and expensive. The potential of the bottom ash as the substitute catalyst in biomass steam gasification is discussed, thus the characterization of the bottom ash is performed to determine the surface morphology, chemical compound, pore size, pore volume, surface area and bulk density of the bottom ash. The result shows that the bottom ash contains elements such as SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO which have been used as the catalyst in biomass steam gasification. The pore volume of the bottom ash is 3.01 nm which falls into mesoporous category and the pore volume is 0.04 cm^3/g with surface area of 58.01 m^2/g and bulk density of 2.53 g/cm.

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Keywords: Biomass gasification; catalyst; bottom ash; characterization

1. Introduction

Biomass gasification is one of the possible alternatives for renewable energy and has received a lot of attention in recent years. It is considered to be a tool to reduce the green house gasses (GHG) emissions because life cycle of biomass confirms the CO_2 neutrality [1]. However, the product gas quality and the formation of by-product are still the problems that need to be solved for commercialization. The product gas quality is affected by many factors such as catalyst, reactor type and gasifying agent type.

The product gas quality can be improved to some extent by use of catalyst in the gasification. Thus, the catalytic gasification is considered to be the most promising method for biomass gasification to enhance the product gas quality [4, 5]. The research interest in catalytic gasification has grown considerably due to tar elimination and removal of unwanted product to ensure economic viability [2]. Usually, the catalyst used in biomass gasification must effectively reduce or remove the tar, reform the methane in case of hydrogen and syngas production, achieve desired gas ratio formation of different fuel and chemicals, have

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long active life and resist carbon deposition to avoid sintering, be strong enough to maintain it property at high temperature and have capacity for low cost regeneration [2, 5].

The effective utilization of catalyst depends on the placement of catalyst within the process. Some catalysts are known as the primary catalysts are placed in first reactor to enhance the gasification process. This type of catalyst enhanced process carbonation, combustion, methanation and reforming reaction, and reduced the tar formation for effective conversion of organic compounds into gases [2, 6]. On the other hand, some catalysts are placed in downstream reactor to enhance the reaction involved in the formation of desired products like hydrocarbon and methane. These are known as secondary catalyst. The operating conditions for primary catalyst are similar as gasification. Whereas secondary catalysts are operated of different conditions other than that of gasification [2].

Generally, the catalyst used in biomass gasification can be divided into three main categories which are natural mineral catalyst, alkali metal catalyst and transition metal catalyst [2, 5]. The natural mineral catalyst is relatively cheap and disposable. The most commonly used natural minerals catalyst are limestone (CaO), dolomite ($MgCO_3.CaCO_3$) and olivine ($(Mg.Fe)_2SiO_4$). These types of catalyst are the common catalysts used in biomass gasification due to low price, easy to dispose and have good ability to remove tars from the product gas [7]. Nickel (Ni) is the most popular transition metal catalyst and extensively used in biomass gasification due to its ability to reduce tar and improve the quality of the product gas. The versatility of nickel catalyst makes it economically attractive for in-situ process development because it can reduce the plant capital and operating cost [5, 8]. Due to its rapid loss of activity, several attempts have been made to improve nickel based catalyst performance by adding metal promoter and support materials into the catalyst such as olivine, dolomite [9], alumina [9-11], silica [9-11], iron, cobalt [5, 12] and magnesium oxide [10].

Alkali metals such as lithium (Li), sodium (Na) and potassium (K) are highly reactive and exist in lesser extent in the biomass which release and vaporise at high temperature during gasification [13]. It also can be used directly with the biomass or impregnated with catalyst support or with ash produced in gasification itself [2, 14]. Studies have been made to use these alkali metals as catalysts for biomass gasification. It was reported that they can cause considerable increase of the product gas but these catalysts are susceptible to loss of activity due to agglomeration inside the gasifier [5, 15]. From the above discussion it could be concluded that catalysts are very important in gasification process. Currently, all types of catalysts have advantages and disadvantages. It is agreed that new and cheaper catalyst is required for gasification process to be economical.

Bottom ash is a waste product for coal power plants. The characteristics of the bottom ash also make it as an alternative material for road construction especially in foundation and asphalt concretes [16]. In recent research, bottom ash has been tested to replace the common noise barrier used to minimize the sound reflection towards noise sensitive areas near the highway [17]. The results show that the bottom ash provides good noise absorption characteristics with the potential to be used commercially near the noise sensitive area. Despite the research on the usage of the bottom ash stated above, the bottom ash is still being disposed rather than recycled as useful products. The traditional method for disposal of the solid waste is land filling and pond disposal. However it is classified as hazardous material due to its high chloride and heavy metal content resulting in possible environmental pollution to the land fill and pond area [18, 19]. The land filling and pond disposal method are not sustainable as new land and pond needs to be acquired once the existing land and pond reaches its capacity [20].

Research has been done to identify the chemical composition of the bottom ash. The primary components of bottom ash are silicon oxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO) and carbon (C) [21, 22]. There are other components present in the bottom ash but in low proportion. Usually, bottom ash account for 60% to 90% of the total ash generated [23]. The chemical characteristics of ash varied depending on the type of fuel burned and also the temperature they are subjected to [21]. These variations of characteristics make the bottom ash highly heterogeneous. Table 2 below shows the chemical composition of several bottom ash samples by means of X-Ray Fluorescence (XRF) method from previous research.

Bottom ash contains Fe, Al, Ca, Mg, K and Na which are used as a catalyst in gasification. It could therefore be utilized in gasification. Xiong et al. used bottom ash in coal gasification as bed material by using air as gasifying agent. The result shows that the mineral presence in the bottom ash are responsible in tar reduction while producing low amount of CO_2 in the product gas [24]. According to authors knowledge, bottom ash has not been investigated in the light of its used as a catalyst in biomass gasification. The purpose of this study is to investigate the bottom ash of Malaysian power plant characteristics, its composition and other physical properties to determine it potential in biomass gasification.

2. Material and Method

The bottom ash is collected from a landfill in a coal power plant situated in Perak, Malaysia. The bottom ash is sun dried for a day and then further dried in an air oven at 100 °C for 24 hours. The dried samples were grounded using Fritsch Analytical Mill 19/25 and sieved to particle size of <250 µm.

2.1 Surface Morphology and properties

The morphological study of the bottom ash is performed using Oxford LEO 1430 Field Emission Scanning Electron Microscopy (FESEM). Electron beam is used to reflect the atom present in the material and the magnifications of the images are 1000 times and 5000 times. Brunauer-Emmett-Taylor (BET) technique is used to study the characteristics of bottom ash pores and to determine if it is a microporous, mesoporous or macroporous material. Other measured properties include pore size, pore volume and surface area. The measurement is conducted using Physisorption Analyzer Micromeritics ASAP 2020. The bulk density of the bottom ash is determined using Ultrapycnometer 1000. The bottom ash was weight first before helium gas is injected into the chamber to determine the bulk density of the bottom ash.

2.2 Composition

In order to identify the elements and determine the compound present in bottom ash of Malaysian coal power plants, the sample is analysed using Bruker AXS XRF S4 Pioneer X-Ray Fluorescence (XRF). The sample size is maintained at 0.250 mm which is the normal size of catalyst used in gasification.

3. Result and Discussion

3.1 FESEM analysis

The FESEM images of the bottom ash in 1000 times magnification and 5000 times magnification are represented in Figure 1 (a) and 2 (b) respectively. Figure 1 (a) shows the surface image of the bottom ash at 1000 times magnification and it shows that the bottom ash consists of mixture of fine and coarse grains particles with no particular pattern. At 5000 times magnification, clearer image of the spherical, rectangular and irregular shapes bottom ash particles is measured. Moreover, the surface of the particle was observed to be mixture of irregular and porous. The porous particles indicated that the bottom ash experienced melting and volatile was released during the combustion of the coal [25]. The irregular and porous structure shows that it could provide surfaces for better contact of biomass gasification agent.

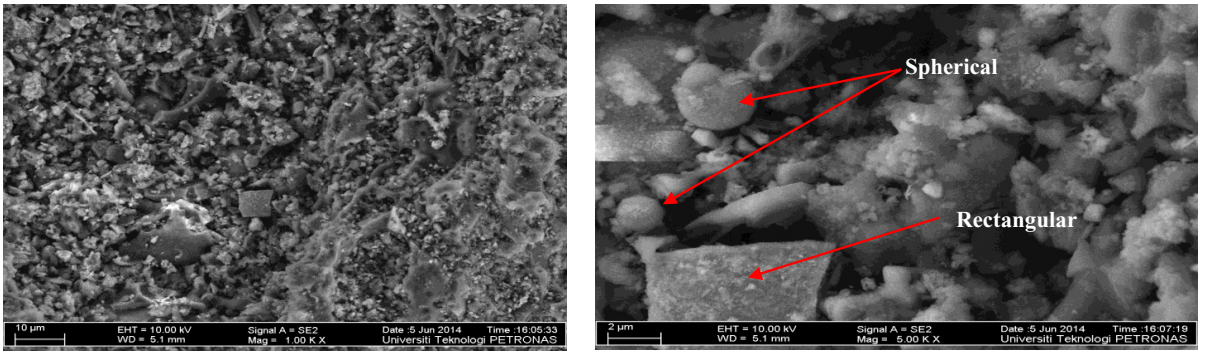

Figure 1. (a) Surface image of the bottom ash at 1000 times magnification; (b) Surface image of the bottom ash at 5000 times magnification.

3.2 XRF analysis

The aimed of the XRF characterization is to identify the elements present in the bottom ash as shown in Table 1. The presense of Fe , Ca , K are in good percentage that enable it to be used as a catalyst in gasification. From the table, Fe is the most abundant element in the bottom ash with 36.1 wt %, followed by Si with 31.0 wt % and Ca with 16.4 wt%. Other elements such as K, Mg, Ti, P and Na make up the rest of the composition with less than 2 wt % respectively. The presense of oxides and thier composition is determined and compared with previous reported composition as shown in Table 2. The result showed that major component of the bottom ash is 44.1 wt% SiO_2 followed by Fe_2O_3, CaO and Al_2O_3 which are 25.3 wt%, 13.0 wt% and 9.31 wt% respectively. Other than that, compound such as MgO, P_2O_5, TiO_5, K_2O and SO_3 existed in the bottom ash in lesser amount of 1.88 wt%, 1.57 wt%, 1.42 wt%, 1.25 wt% and 1.05 wt% respectively. Other metal oxides such as BaO, MnO, V_2O_5, NiO, ZrO_2, ZnO and SrO collectively contribute less than 1 wt% of the sample composition. The main compounds present in the bottom ash has been used in biomass gasification before. SiO_2 is mostly used as bed material, while Al_2O_3 and Fe_2O_3 help to resist the carbon deposition and sintering of Ni catalyst in the in-situ process.

Table 1. Elemental composition of coal bottom ash from XRF analysis

Element	Concentration (wt %)
Fe	36.09
Si	30.89
Ca	16.39
K	1.92
Mg	1.62
Ti	1.53
P	1.04
Na	0.61

Table 2. Comparison of chemical composition of previous and present study from XRF.

Component	Present study	Carssco et al. [21]	Areans et al. [17]	Zarmeno et al. [19]	Meawad et al. [26]
SiO2	44.01	27.87	52.32	43.31	53.68
Al_2O_3	9.31	4.34	25.15	5.81	18.91
CaO	13.01	29.96	2.37	16.91	1.21
Fe_2O_3	25.03	3.59	9.23	14.11	7.71
MgO	1.88	4.05	1.84	2.22	0.48
K_2O	1.25	23.22	3.72	1.11	0.23
Na_2O	-	0.35	0.66	7.58	0.05

CaO helps to absorb the CO_2 produced from the gasification thus increasing the quality of the product gas as used by many researcher [1, 27]. Dolomite is a very important catalyst in biomass gasification to reduce tar formation and increase the product yield. It is derived from calsium and magnesium ore. Notably, both elements exist in the bottom ash.

3.3 Surface area and density analysis

BET analysis technique is used to study the characteristics of the sample pores such as pore size, surface area and to determine whether the sample is microporous, mesoporous or macroporous. From the analysis, the pore width of the bottom ash is 3.01 nm which falls under mesoporous group. Mesoporous particle mainly contributes around 2 – 50 nm [28]. The pore volume of the bottom ash is 0.04 cm^3/g that is higher than Ni and CaO 0.019 and 0.0016 as reported by Khan et al. [29] while the surface area of the bottom ash is 58.01 m^2/g that is higher compare to the surface area of Ni and CaO as reported by Khan et al. The larger surface are is good for CO_2 adosrption [29]. The bulk density of the bottom ash is 2.53 g/cm^3 is higher than quicklime but closed to silica. It shows that it could replaced the SiO as a bed material in gasification and has additional advantage as catlaytic effect with respect to the gas composition as evidented by XRF analysis in Tables 1 and 2.

Table 3. Density and surface properties of the bottom ash

Parameters	Results
Pore Width (nm)	3.01
Pore Volume (cm^3/g)	0.04
BET Surface Area (m^2/g)	58.01
Density (g/cm^3)	2.53

4. Conclusion

Bottom ash is a waste product from the coal power plant and from its characterization, it shows that bottom ash has good potential to be used as catalyst in biomass steam gasification. The elements present in bottom ash such as Si, Ca, Mg, Fe, Al and Ti confirm its potential to be used as catalyst since these elements have been used as the catalyst for biomass gasification. The huge amount of SiO_2 indicates that the bottom ash could also be used as bed material for in-situ process, Fe_2O_3 can enhance the

tar reduction in product gas while the presence of CaO helps to increase the product gas yield by decreasing the carbon dioxide content. The surface area of 58.01 m^2/g makes bottom ash a good option for CO_2 adsorption in gasification. The bottom ash is a waste so its utilization makes the process to be more economical viable due to its low cost and abundance.

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